Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

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Abstract

Human and ecological risk assessments of contaminated soils rely on models that link soil residue levels to exposure concentrations in edible plant parts. Currently, these models use empirical relationships developed from a relatively small number of plant species and chemicals. Uptake into vegetation is often assumed to follow a simple plant-soil partitioning relationship, which can miss the influence of transformation processes and variations among vegetation types. As a result, linking chemical residues in soil to exposure concentrations in food or feed is highly uncertainty and very little quantitative information is available for reducing this uncertainty. In the first year of this partnership we reviewed the literature to identify existing data and theory that could be used to develop a revised, semi-mechanistic plant uptake model. The revised model and existing data indicate that the most commonly used empirical models for plant uptake over-predict the amount of chemical that is likely to accumulate in vegetation from soil, particularly for chemicals that are relevant to the petroleum industry. Controlled exposure studies are underway to collect data to improve our understanding of the mechanistic basis of plant uptake. This poster describes progress made during fiscal year 02 and experiments currently underway or planned for FY03 and 04.

Background

Recent efforts by the Petroleum Environmental Research Forum (PERF) (e.g. PERF 94-06, 97-08 and 99-13) have focused on the use of risk and science-based methods to identify total petroleum hydrocarbon (TPH) clean-up levels in soil. Uncertainties about the links between soil residue levels and human or ecological exposures lead to conservative risk assessment assumptions that result in regulatory decisions to set allowable soil residues at low levels. When measured biotransfer factors (BTFs) are lacking, which is most often the case, empirically-based models derived from a limited number of chemicals (mostly chlorinated hydrocarbons) are used to link soil residues to exposure concentrations in food or feed. The same empirical relationships are used in all existing regulatory environmental modeling frameworks (i.e., TRIM.FaTE, 3MRA, IEM-2M, Eco-SSL). Although a number of published reviews relating to various aspects of plant uptake are available, existing technologies (i.e. models and databases) for estimating biotransfer have not been evaluated for applicability to petroleum hydrocarbons.

Problem Statement

Without quantitative information to reduce uncertainty in the relationship between chemical residues in soil and exposure concentrations in food or feed, models of ecological and human risk will remain highly conservative leading to excessively low risk-based residue levels.

Objectives

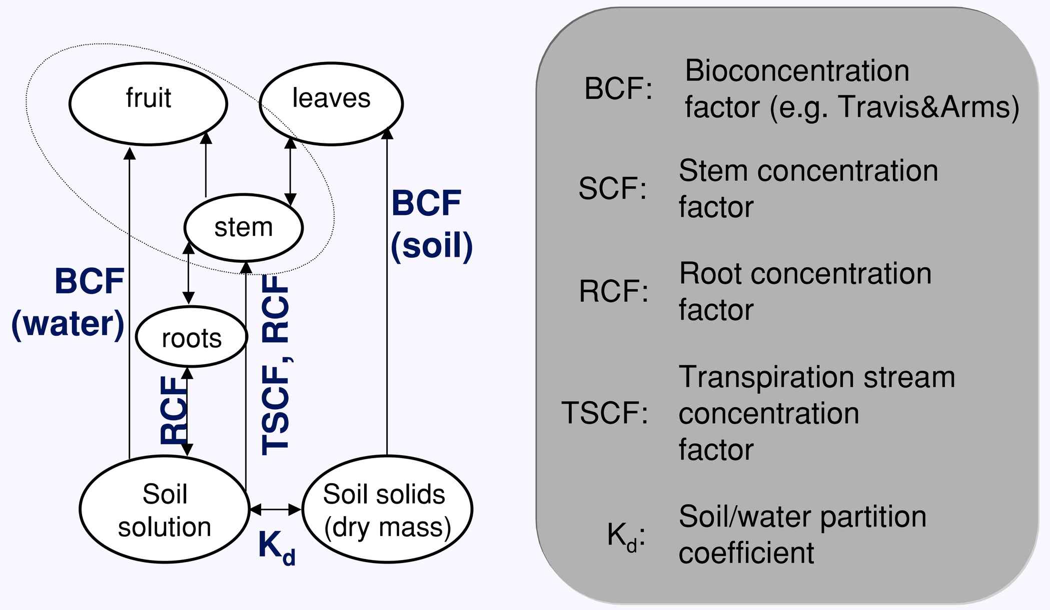
Our overall objective is to reduce uncertainty in plant uptake models for petroleum contaminated soils thereby increasing reliability and acceptability of risk-based methods.

1) characterize the state of the art of plant uptake modeling with particular emphasis on petroleum contaminated soil
2) identify and collect experimental plant uptake data using a controlled exposure system
3) develop a semi-mechanistic model for characterizing the transfer of petroleum hydrocarbons from soil to vegetation.

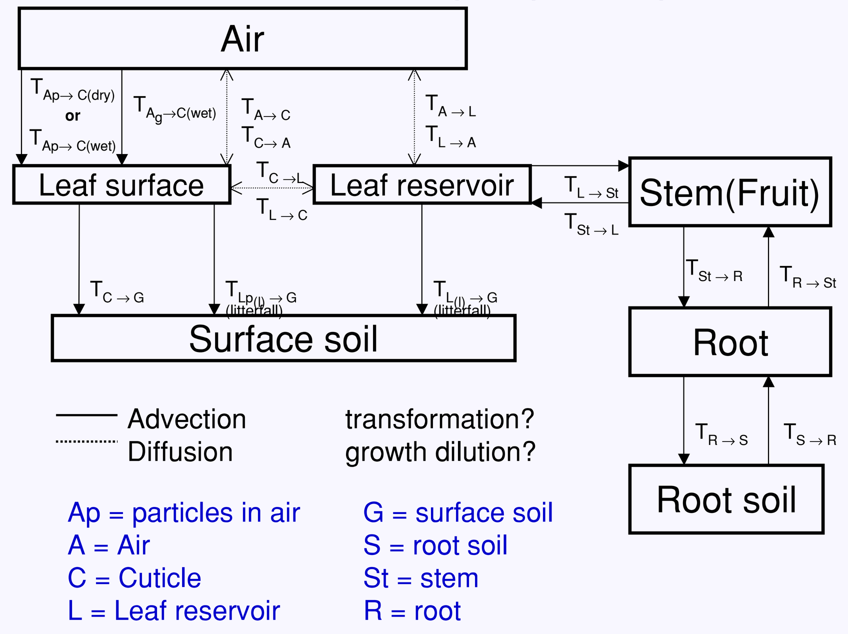
Tasks and Aproach

1. Complete a comprehensive review of the scientific literature for plant uptake culminating in a revised semi-mechanistic plant uptake model for use in identifying critical data gaps. The revised model is incorporated into a multimedia fate and transport modeling framework providing a fully coupled soil-plant-air system. The effort provides the basis for comparing existing tools, which are used to support regulatory decisions, to the range of mechanistic, theoretical and empirical models that are available to describe plant uptake.
2. Design and perform controlled experimental exposure chamber studies to better characterize the mechanistic basis of plant uptake for petroleum residues in soil. The experiments build upon two existing exposure chamber designs that were developed through collaborations between LBNL and the University of California. The chamber studies provide a unique opportunity to examine the combined role of uptake and transformation in plants under relevant exposure duration and conditions. Initial exposure studies focus on a series of polycyclic aromatic hydrocarbons in wheat grown in a sandy loam soil.
3. Apply results from chamber studies to begin to characterize the mechanistic basis of plant uptake and develop or recommend an approach for evaluating the transfer of petroleum hydrocarbon residues from soil into food chains. Measured bioconcentration ratios for the initial set of test chemicals will be reported through peer-reviewed journals, conference proceedings and workshop participation. The experimental data combined with the ongoing literature review are expected to result in a more reliable and mechanistically based modeling system for plant uptake.

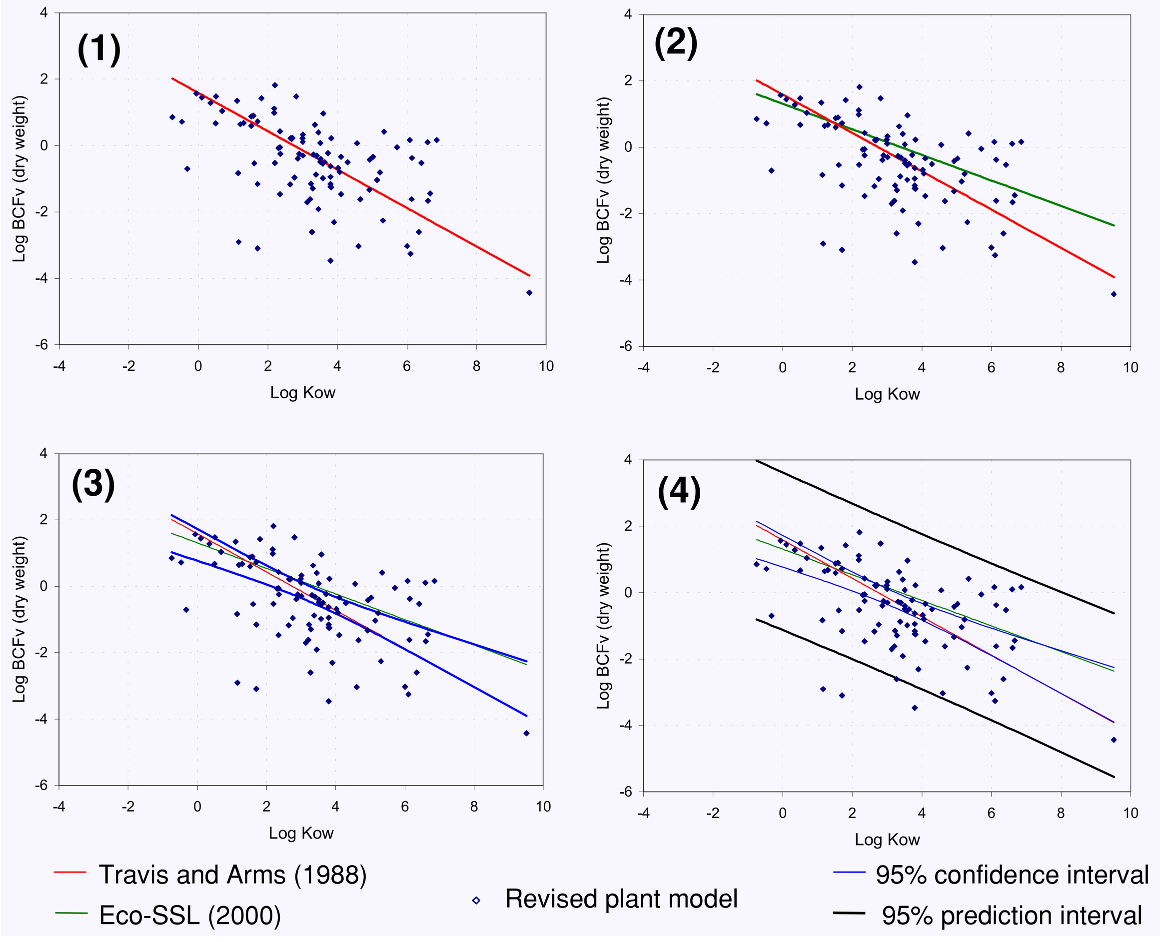
Identification of existing models for plant uptake



Revised model incorporating existing theory and semi-mechanistic understanding of plant uptake.



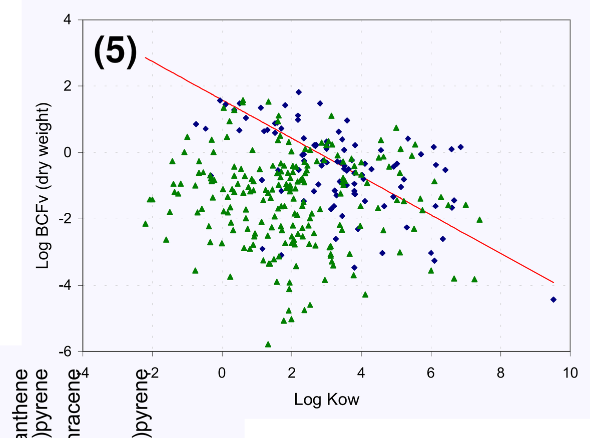
Comparison of predicted soil-plant bioconcentration factors (BCFv) for **pesticides and chlorinated hydrocarbons**



The blue diamonds in this series of figures are BCFv predictions from the revised model using chemicals relevant to the original training set for existing empirical models. The red line in **Figure 1** represents the original model by Travis and Arms (1988). Recently the EPA re-evaluated the Travis and Arms model and published a new curve illustrated by the green line in **Figure 2**. To compare our predictions to these existing models we estimate the 95% confidence interval for the regression through the BCFv (blue line in **Figure 3**) and find that the three models are not significantly different. However, it is important to note that for both of the empirical models (Travis and Arms and the Eco-SSL), the 95% confidence interval for the predictions cover ~ 4 orders of magnitude (black line in **Figure 4**).

Model comparison with full set of ~300 chemicals

When all chemicals are included in the comparison we find that for non-pesticide chemicals including VOCs, solvents, PAHs, alkanes, etc., (green triangles in **Figure 5**) the predictions from the revised model deviate significantly from the Travis and Arms model.



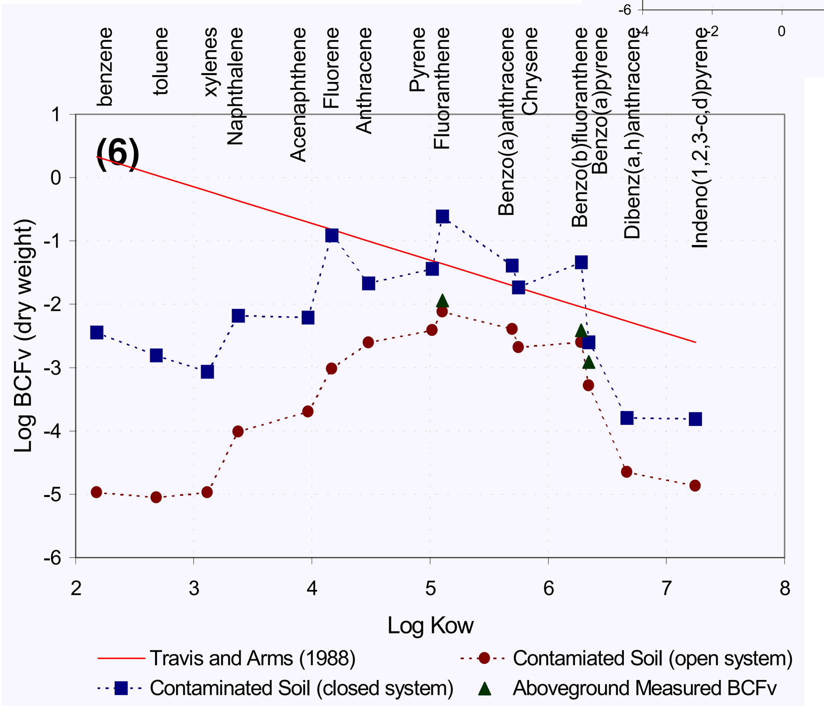


Figure 6 focuses in on the BTEX and PAH series with log Kow range 2 - 8 using both an open system (red circles) and a closed system (blue squares). The open system includes competing loss pathways (i.e., advection or degradation in other media). Also illustrated are measurements from Petersen et al (2002) shown as black triangles.

Selection of plant/soil combination and experimental design

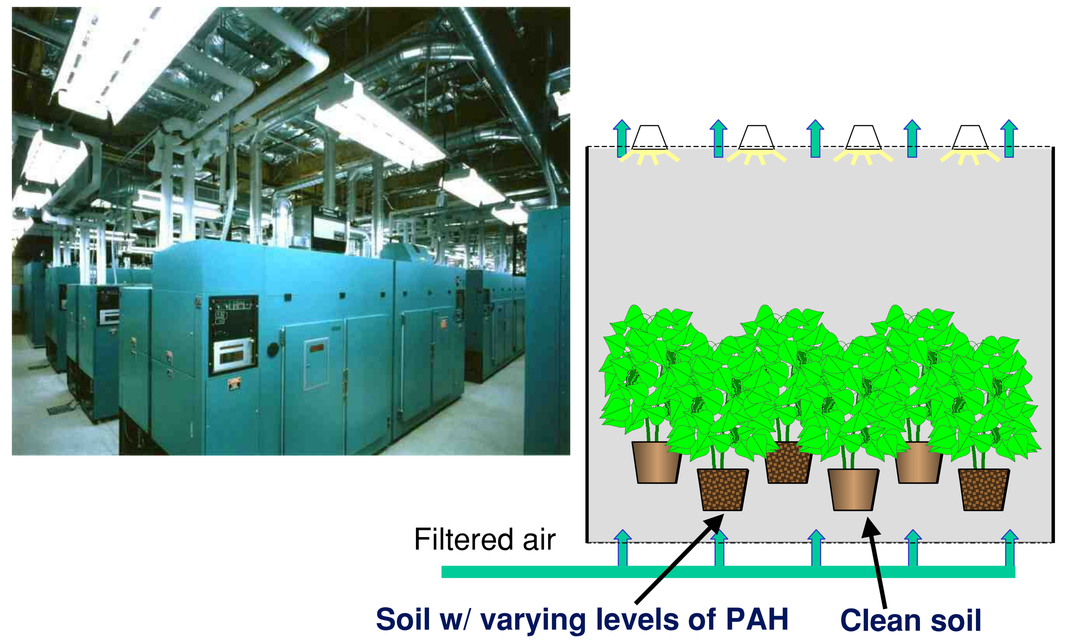
Lifetime Average Daily Intake of Foods*

Food Category	*g/kg/d*	*CV*
Leafy produce	0.56	0.75
Exposed produce	2.16	0.65
Protected produce	1.92	0.41
Root produce	1.21	0.23
Grain	3.83 (16.1)	0.14
Vegetable based fat/oil	0.23 (4.9)	0.4
Meat	2.07	0.12
Dairy	6.57	0.45
Fish	0.34	0.2
Eggs	0.30	0.62

- When converted to fresh weight, total grains contribute > 70% of the daily intake of plant-based foods
- Grains provide a useful surrogate for animal feed and forage
- total grain in the diet is ~ 75% wheat
- wheat grain is a "protected" crop, which will minimize background from atmospheric PAH
- Grain may be more relevant to E&P sites than garden vegetables
- Sandy/loam agricultural soil was selected as a representative soil for grains
- Methods for chemical extraction using a pressurized liquid extraction method, cleanup with gel permeation and silica column and analysis with GC/MS have been developed for PAH in wheat

* Mass reported "as consumed". For grain and oil the fresh field weight is listed in parentheses.

Experimental system for study of plant uptake



Test plants are grown in sterilized agricultural soil spiked with PAH at several contaminant levels (+controls). The filtered exposure system excludes ambient PAH from the chamber. Soil, air and plant tissue are sampled at regular intervals during growing season. Results provide information on kinetics, thermodynamics and mass balance for plant uptake.

Summary and Discussion

- Existing models of plant that tell what is possible, not necessarily what is likely
- First stage of literature review completed and results include a revised model incorporating the state of the art in plant uptake modeling (literature review to continue for duration of project)
- Revised model used to evaluate existing empirically-based models with particular emphasis on chemicals relevant to the petroleum industry - existing empirical models overestimate plant uptake relative to revised model, targeted studies needed evaluate reason for difference
- Controlled experiments are underway to characterizing mechanistic basis of plant uptake and further evaluate/develop model that is appropriate for petroleum contaminated sites
- These experiments expected to provide data that will reduce uncertainty in the plant uptake component of risk based methods